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UNDERSTANDING THE CHEMISTRY OF UNCOMMON AMERICIUM OXIDATION STATES FOR APPLICATION TO ACTINIDE/LANTHANIDE SEPARATIONS

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A spectroscopic study of the stability of Am(V) and Am(VI) produced by oxidizing Am(III) with sodium bismuthate is presented, varying the initial americium concentration, temperature and length of the oxidation was seen to have profound effects on the resultant solutions.

I. INTRODUCTION

The aqueous chemistry of americium is primarily concerned with the Am(III), Am(V) and Am(VI) ions, with the latter two species being in the form of the well documented "actinyl" unit.[1] Although evidence for Am^{4+} has been obtained, it only exists in highly complexing media such as 13 M NH_4F and solutions containing polyoxometalate ions.[2] As with the other actinide elements each of the americium ions have distinct electronic absorption spectra consisting primarily of sharp *f-f* transitions.[3] The availability of these higher oxidation states is important from a separations standpoint, both in spent nuclear fuel processing and national security applications.[4] Although the +5 and +6 oxidation states are available, their reduction potentials of E°(III/V) = +1.73V, E°(III/VI) = +1.68V in 1.0 M $HClO_4$ mean that oxidized Am species are powerful oxidants themselves and hence long term stability is problematic.[5] Maintaining any elevated oxidation state to allow the development of a separation technique, or simply for studying its fundamental chemistry is particularly challenging.

Aside from electrolytic oxidation, there are two classical methods for the oxidation of Am^{3+} to these unconventional oxidation states, the use of ozone and persulfate.[6a] Unfortunately both come with drawbacks, ozone will not directly oxidize Am(III) to Am(VI) and persulfate will not completely oxidize Am(III) above 0.5 M H^+ due to the hydrolysis of the $S_2O_8^{2+}$ ion. It has come to our attention that sodium bismuthate could also be used for this purpose. However, characterization of the resultant solutions, and the chemistry of the oxidized species is inadequately described.[6]

In this study, we have primarily used sodium bismuthate ($NaBiO_3$) as the oxidant to produce solutions of Am in the +5 and +6 oxidation states. We were able to achieve these results by using a delicate interplay of the oxidizing power of $NaBiO_3$ and the complex aqueous chemistry of americium. The results of these oxidations were studied by UV-vis-nIR spectroscopy using both a conventional 1 cm cell and a 100 cm Liquid Waveguide Capillary Cell. These results allowed for a re-evaluation of the extinction coefficients of the major Am(VI) absorption bands in HNO_3 media.

II. EXPERIMENTAL

All UV-visible spectra were recorded using a Varian Cary 50 Bio spectrophotometer with a fiber optic coupler. Spectra generated from solutions where [Am] = 2.41×10^{-3} M were collected using a reduced volume 1 cm pathlength cell and spectra generated where [Am] = 3.60×10^{-5} M were collected using a Liquid Waveguide Capillary Cell (World Precision Instruments) with an effective pathlength of 1 m. Despite the wavelength range of the spectrophotometer being 200-1100 nm data collection was restricted to 450-750 nm due to the absorption of water in the 1 m pathlength cell. The oxidation of Am(III) to Am(V) and Am(VI) in 0.5 M nitric acid was performed by adding 40 mg of sodium bismuthate ($NaBiO_3$) powder to 5 mL of 0.5 M nitric acid. The ^{243}Am was from stock on hand at the Idaho National Laboratory (INL). Chemicals were used as received without any further purification. Oxidations carried out at elevated temperatures (87 ± 1ºC) were performed in a waterbath with manual agitation over the course of the experiment.

III. RESULTS AND DISCUSSION

After shaking a solution of 3.6×10^{-5} M Am in 0.5 M HNO_3 with 40 mg of $NaBiO_3$ for two hours at 25 ± 1°C the electronic absorption spectra shown in Figure 1 were obtained, showing the presence of Am(III), Am(V) and

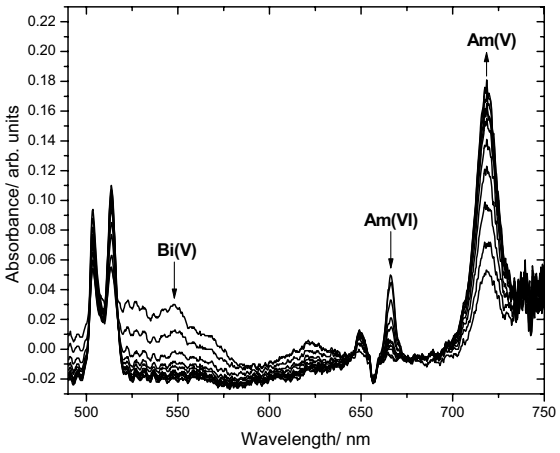

Fig. 1. UV-visible spectra of an Am solution oxidized using $NaBiO_3$. $[Am]_{initial}$ $3.6x10^{-5}$ M measured using a 100 cm pathlength cell.

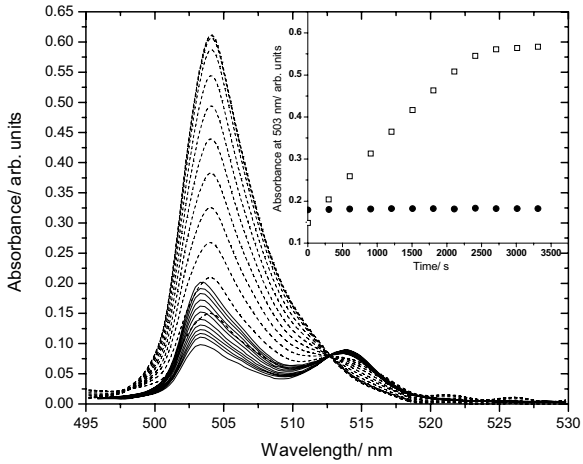

Fig. 2. Electronic absorption spectra of the reduction of Am(V) when produced by persulfate (grey dashed traces) and $NaBiO_3$ (black solid traces). Insert depicts the ingrowth of Am(III) over 40 mins for solution treated with persulfate (□) and $NaBiO_3$ (•).

Am(VI) co-existing in solution. The broad absorbance centered at 525 nm is due to Bi(V) in solution. Over the course of about 40 minutes the intensity of this broad peak decreases corresponding with, albeit slightly delayed, the decrease in intensity of the Am(VI) peak. This is a clear indication that the solublized Bi(V) not only oxidizes Am(III) to Am(V) and Am(VI) at room temperature, but also acts as a holding oxidant for Am(VI). Qualitatively these results show that, as expected, the product of the Am(VI) reduction is Am(V). These results are significant as this is the first direct evidence for not only the production, but also the stability of Am(V) and Am(VI) at micro molar concentrations. Using what was considered the best extinction coefficients available for these species it was calculated that the solution contained *ca*. 59% Am(VI), and 35% Am(V) (using the peak at 717 nm)[7] immediately after oxidation.

An accurate determination of the percentage of Am(III) present was not possible due to the interference of the Bi(V) absorption. This solution was further monitored via UV-vis spectroscopy, expecting to investigate the rapid reduction of the resultant Am(V) to Am(III). The results were somewhat surprising, there was found to be little reduction of Am(V) to Am(III) over a period of 24 hours. This result is of particular interest when considering what is predicted by Am(V) disproportionation kinetics, as significantly faster rate of reduction would be expected.[8] When performing an oxidation experiment in the same background electrolyte, using the persulfate/ Ag(II) preparation method, the initial electronic absorption spectrum recorded established that the solution contained only Am(III) and Am(VI). The Am(VI) produced via this method was slightly more stable than that produced when using $NaBiO_3$ as the oxidant. When all of the Am(VI) had been reduced to Am(V), electronic absorption spectra were recorded every 5 minutes, Figure 2 (grey dashed traces). The Am(V) proceeded to reduce to give a solution of Am(III) in 40-45 minutes. The isosbestic point obtained at 512.5 nm suggests that there are only two absorbing species involved in this reaction, with respect to the limitations of this argument.[9] This reduction pathway is similar to what is observed in HCl. In the reducing HCl media, the Am(V) reduction proceeds more rapidly than in non-complexing perchlorate media and with no observation of Am(VI) ingrowth. The persulfate results are in stark contrast to the behavior observed for the reduction of Am(V) prepared in nitric acid media but oxidized using $NaBiO_3$. Figure 2 also shows the electronic absorption spectra obtained from a $NaBiO_3$ treated solution recorded at 50 minute intervals (black solid traces). Again an isosbestic point was observed at 512.5 nm. The inset demonstrates that in the same time period that it takes for Am(V) to be completely reduced when produced by oxidation with persulfate, by monitoring the ingrowth of Am(III), there is no significant observable change in Am(III) concentration with the Bi(V) treated solution over the same time period.

To directly compare results with the persulfate oxidation a sample of Am was heated with the Bi(V) at 87 ± 1°C for one hour. The result of this method of oxidation was a solution of pure Am(V), Figure 3. In addition there was no evidence of any reduction of Am(V), by the ingrowth of the Am(III) peak for at least 24 hours. To compliment this study, a similar

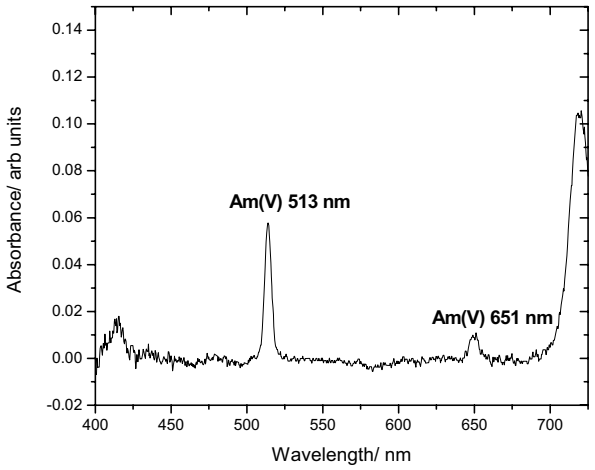

Fig. 3. Ultraviolet-visible absorbance spectrum for $1.3x10^{-5}$M Am solution following oxidation with sodium bismuthate at 87°C, showing quantitative production of Am(V), in 0.5 M HNO_3.

investigation was performed at a higher Am concentration, $2.41x10^{-3}$ M from γ-counting, allowing for a 1 cm cuvette to be used instead of the 100 cm Liquid Waveguide Capillary Cell. When using a higher initial concentration of Am, and oxidizing with Bi(V) at room temperature for 2 hours the resulting solution composition was primarily Am(VI) with a small quantity of Am(III) still present.

Using the reported extinction coefficient of 391 L mol^{-1} cm^{-1},[7] the concentration of Am(III) in the solution was determined to be $1x10^{-4}$ M approximately equating to 4% of the total americium in solution, Figure 3. It became apparent when using previously determined extinction coefficients for the 666 and 994 nm peaks of Am(VI) to calculate the concentration did not result in a congruent concentration.[7] The extinction coefficients for these peaks were re-calculated using the total Am concentration corrected for the concentration of Am(III) present. For the peak at 666 nm the ε was found to be 23.70 L mol^{-1} cm^{-1} and for the peak at 994 nm ε was determined as 98.84 L mol^{-1} cm^{-1}. These extinction coefficients were then applied to other spectra of Am(VI) in nitrate media gathered from our Laboratory and found to be more internally consistent, Table 1.

An increased proportion of Am(VI) was produced when oxidizing the Am solution with an initial concentration of $2.41x10^{-3}$ M with $NaBiO_3$. The Am(VI) generated persisted in solution in excess of 8 hours. In addition, the Am(V) produced from the reduction of Am(VI) remained in solution for an unusually long period of time. The electronic absorption spectra of this solution recorded one week later did not show any evidence for

TABLE I. Calculated concentrations, and relative ratios, of Am(VI) as it reduces determined using the newly defined extinction coefficients of 98.84 L mol^{-1} cm^{-1} and 23.70 L mol^{-1} cm^{-1} for the 994 and 666 nm peaks respectively.

994 nm		666 nm		
Abs./ arb. Units	Calculated Conc./ M	Abs./ arb. Units	Calculated Conc./ M	Conc. ratio
0.1807	$1.83x10^{-3}$	0.0423	$1.78x10^{-3}$	1.03
0.1804	$1.82x10^{-3}$	0.0410	$1.73x10^{-3}$	1.06
0.1720	$1.74x10^{-3}$	0.0417	$1.76x10^{-3}$	0.99
0.1760	$1.78x10^{-3}$	0.0414	$1.76x10^{-3}$	1.02
0.1647	$1.67x10^{-3}$	0.0403	$1.76x10^{-3}$	0.97
0.1664	$1.68x10^{-3}$	0.0402	$1.72x10^{-3}$	0.99
0.1608	$1.63x10^{-3}$	0.0378	$1.69x10^{-3}$	1.02
0.1540	$1.56x10^{-3}$	0.0364	$1.59x10^{-3}$	1.02
0.1554	$1.57x10^{-3}$	0.0364	$1.53x10^{-3}$	1.02
0.1474	$1.49x10^{-3}$	0.0341	$1.53x10^{-3}$	1.04
0.1375	$1.39x10^{-3}$	0.0335	$1.42x10^{-3}$	0.98
0.1304	$1.32x10^{-3}$	0.0230	$1.25x10^{-3}$	1.05
0.1266	$1.28x10^{-3}$	0.0302	$1.28x10^{-3}$	1.00

Am(VI) however, Am(V) was still present in solution in appreciable quantities. These results serve to validate those observed using the longer pathlength cell. That is to say the use of Bi(V) as an oxidant results in solutions containing unusually persistent oxidized Am species.

The mechanism by which the oxidized americium species produced from treatment with bismuth(V) display increased stability is still under investigation. We are exploring the possibility of an Am(V)-Bi(III) cation-cation complex that exists in solution that inhibits disproportionation reactions leaving only the kinetically slower auto reduction. Only one cation-cation interaction of Am(V) has been previously reported, but no comment was made on the resultant stability of the Am(V) in these solutions.[10]

IV. CONCLUSIONS

We have demonstrated that the use of $NaBiO_3$ for the oxidation of Am results in solutions containing Am(V) and Am(VI). Changes to the initial Am concentration and temperature at which the oxidation is performed, have profound results on the distribution of Am oxidation states. Any Am(V) produced in this manner is seen to persist in solution longer than any other oxidation method previously reported. In addition new extinction coefficients have been determined for the 666 and 994 nm peaks in the electronic absorption spectra of Am(VI).

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